

# Magnetic and thermal properties of $\text{Ce}_2\text{Pd}_2\text{Sn}$

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## Abstract

X-ray diffraction, susceptibility and specific heat studies on ternary  $\text{Ce}_2\text{Pd}_2\text{Sn}$  intermetallic compound and on its isostructural non-magnetic compound  $\text{La}_2\text{Pd}_2\text{Sn}$  are reported. On  $\text{Ce}_2\text{Pd}_2\text{Sn}$  in absence of magnetic field, we confirm the existence of two magnetic transitions at  $T_N = 4.8$  K (antiferromagnetic transition) and  $T_C = 2.2$  K (ferromagnetic transition) and the specific heat results, measured down to 0.5 K, allow to recognize the transition at 2.2 K as a first-order transition. A description based on molecular field calculations for the  $S = 1/2$  resonant level model leads to a characteristic Kondo  $T_K$  of about 3 K.

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## 1. Introduction

The physics of Rare Earth intermetallic compounds with the magnetic atom located in a non-centro symmetric position has renewed its interest after the recent discovery of the coexistence of magnetism and superconductivity in  $\text{CePt}_3\text{Si}$  [1]. In this type of structures, the anisotropic environment of the magnetic ion provides the conditions for competing magnetic structures that can be favoured by small changes in stoichiometry. Such is the case of the  $\text{Ce}_2\text{T}_2\text{X}$  ( $T = \text{Ni}, \text{Pd}$  and  $X = \text{In}, \text{Sn}, \text{Pb}$ ) family of compounds [2], among which  $\text{Ce}_2\text{T}_{2+x}\text{Sn}_{1-x}$  presents an extended range of solid solution ranging between  $0.04 < x < 0.2$  [3].

The crystal structure of  $\text{Ce}_2\text{Pd}_{2+x}\text{Sn}_{1-x}$  is a derivative of the tetragonal  $\text{U}_3\text{Si}_2$  type, characterized by columns of trigonal and tetragonal prisms surrounding Pd1 and Pd2 (or Sn) atoms, respectively. Consequently, Ce atoms have five nearest neighbours in the basal plane and two along

the “c” axis. The competition between these two magnetic Ce–Ce interactions induces a magnetocrystalline anisotropy leading to peculiar magnetic structures [3]. The local environment of Ce atoms can be described as being surrounded by three trigonal prisms, resembling those of the ferromagnetic-CePd compound and two tetragonal prisms resembling antiferromagnetic-CePdSn compound.

Two magnetic transitions were observed in  $\text{Ce}_2\text{Pd}_{2.04}\text{Sn}_{0.96}$  by  $\chi$  susceptibility measurements. An AF transition was recognized by a cusp at  $T_N = 4.8$  K and a ferromagnetic one at  $T_C = 3$  K determined by a moderate increase of the susceptibility [4]. From neutron diffraction studies, those authors determined that, at intermediate temperature (i.e.,  $T_N > T > T_C$ ), the magnetic structure is incommensurate with  $\text{Ce}^{3+}$  magnetic moments sinusoidally modulated along the tetragonal axis and a propagation vector  $\mathbf{q} = (qx, 0, 0)$  varying between  $0.112 > qx > 0.075$  [4]. Since at  $T_C$   $\mathbf{q} = (qx, 0, 0)$  locks into  $(0, 0, 0)$ , a discontinuity in the thermal evolution of the propagation vector can be expected.

Despite the AF type cusp of the upper transition ( $T_N = 4.8$  K), some other magnetic features suggest a complex interplay of magnetic interactions. Although the high

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Table 1  
Crystallographic and specific heat parameters for  $\text{Ce}_2\text{Pd}_2\text{Sn}$ ,  $\text{Ce}_2\text{Pd}_2\text{Sn}_{1.1}$ ,  $\text{Ce}_2\text{Pd}_2\text{Sn}_{0.9}$  and  $\text{La}_2\text{Pd}_2\text{Sn}$  compounds

Compound	$a$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )	$T_N$ (K)	$T_K$ (K)	$(\delta C_{\text{mag}})(T = T_N)$ (J/K mol Ce)
$\text{Ce}_2\text{Pd}_2\text{Sn}$	7.765 <sup>a</sup>	3.902 <sup>a</sup>	235.3 <sup>a</sup>	4.8 <sup>a</sup>	3.0 <sup>a</sup>	6.0 <sup>a</sup>
$\text{La}_2\text{Pd}_2\text{Sn}$	7.825 <sup>a</sup>	3.955 <sup>a</sup>	242.2 <sup>a</sup>	–	–	–
$\text{Ce}_2\text{Pd}_2\text{Sn}_{1.1}$	7.785 <sup>a</sup>	3.859 <sup>a</sup>	233.9 <sup>a</sup>	4.6 <sup>a</sup>	7.5 <sup>a</sup>	3.15 <sup>a</sup>
$\text{Ce}_2\text{Pd}_2\text{Sn}_{0.9}$	7.762 <sup>a</sup>	3.853 <sup>a</sup>	232.1 <sup>a</sup>	4.5 <sup>a</sup>	6.4 <sup>a</sup>	4.6 <sup>a</sup>
$\text{Ce}_2\text{Pd}_2\text{Sn}$	7.774 <sup>b</sup>	3.926 <sup>b</sup>	237.3 <sup>b</sup>	–	–	–
$\text{Ce}_2\text{Pd}_{2.05}\text{Sn}_{0.95}$	7.762 <sup>c</sup>	3.930 <sup>c</sup>	236.8 <sup>c</sup>	4.7 <sup>a</sup>	3.3 <sup>a</sup>	5.7 <sup>a</sup>

<sup>a</sup>This work.

<sup>b</sup>Ref. [2].

<sup>c</sup>Ref. [5].

temperature ( $T > 100$  K) extrapolation of the inverse magnetic susceptibility indicates a negative Curie–Weiss temperature, a negative curvature below 100 K ends at around 4.8 K [3]. The electrical resistivity  $\rho$  shows a maximum at this temperature after undergoing a minimum at  $\sim 20$  K. Both features, the increase of the electronic scattering down to  $\sim 7$  K and the coherence effect below that temperature are typical of Kondo (usually AF) systems. However, if the temperature of the  $\rho(T)$  maximum is computed as the Kondo temperature (i.e.,  $T_K \sim 7$  K), it would be unlikely to have a ferromagnetic-ground state as it seems to occur in this compound.

With these questions in mind, we have performed low temperature study of  $\text{Ce}_2\text{Pd}_2\text{Sn}_{1.1}$ ,  $\text{Ce}_2\text{Pd}_2\text{Sn}$  and  $\text{Ce}_2\text{Pd}_2\text{Sn}_{0.9}$  samples, in order to determine the  $T_C$  transition, the temperature dependence of the specific heat between  $T_C$  and  $T_N$ , and the  $T_K$  value from the amplitude of the specific heat jump at 4.8 K.

## 2. Synthesis and X-ray powder diffraction

The polycrystalline Ce and La samples were prepared by conventional tri-arc melting of an appropriate amounts of pure Ce(4N), La(4N), Pd(4N) and Sn(4N), under a high purity argon atmosphere on a water-cooled copper hearth. The buttons were remelted several times to ensure good homogeneity. The weight losses after arc melting were lower than 0.2 wt% of total mass (about 1 g for both samples); thus, the alloy compositions were assumed to be the nominal ones. The samples were annealed 3 weeks at 750 °C in a quartz tube sealed under dynamic vacuum. The crystallographic structure of these alloys were checked at room temperature using a Siemens D-5000 X-ray powder diffractometer with monochromatic  $\text{Cu K}\alpha_1$  radiation and a setting of 35 kV and 25 mA. The surface of the samples was mechanically cleaned by scraping slightly with a diamond file in a gloved box under argon gas flow. After this cleaning procedure, the samples were crushed under  $\text{C}_6\text{H}_{12}$  with average grain size  $\leq 5$   $\mu\text{m}$ . This annealing leads to the disappearance of some extra peaks and less unfolding. The peak positions and major peak intensities are all consistent with those expected for materials in the  $\text{U}_3\text{Si}_2$ -type tetragonal structure. X-ray diffraction (XRD)

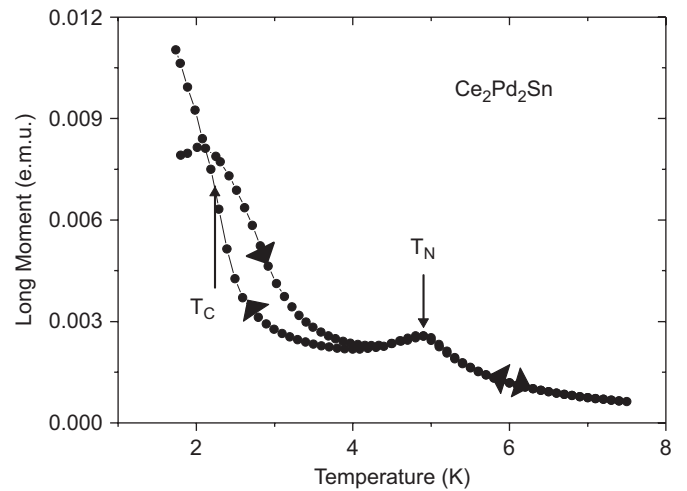


Fig. 1. Magnetic susceptibility of  $\text{Ce}_2\text{Pd}_2\text{Sn}$  on cooling and heating from 1.8 to 7 K.

patterns for Ce and La compounds can be indexed to a tetragonal cell with the lattice parameters given in Table 1, in good agreement with the literature data [2,5].

## 3. Magnetization measurements

The susceptibility measurements were carried out using a superconducting quantum interference device (SQUID) magnetometer. Fig. 1 shows the magnetic susceptibility for  $\text{Ce}_2\text{Pd}_2\text{Sn}$  as a function of temperature in the 1.8–7 K range; we observe two distinct anomalies and an hysteresis behaviour:

- a sharp maximum around  $T_N = 4.9$  K suggesting the occurrence of an AF phase transition, which will be confirmed from the magnetization in magnetic field measurements;
- at lower temperatures the susceptibility increases with decreasing temperature and presents a thermal hysteresis. This indicates a tendency toward ferromagnetism that means some weak ferromagnetic interactions in the presence of the dominant AF correlations. The Curie temperature can be defined by the inflection

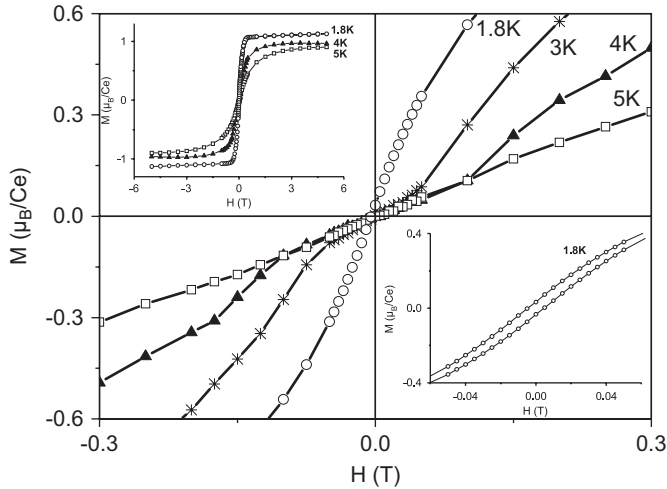


Fig. 2. Magnetization of  $\text{Ce}_2\text{Pd}_2\text{Sn}$  versus magnetic field for  $T = 1.8, 3, 4$  and  $5$  K. Inset: left,  $H \leq 6$  T; inset: right,  $H \leq 50$  mT.

point of the  $\chi(T)$  curve, the  $(d\chi/dT)$  analysis yields  $T_C = 2.2$  K.

Fig. 2 illustrates the magnetization curve measured as a function of magnetic field for  $\text{Ce}_2\text{Pd}_2\text{Sn}$ . As the temperature is lower than  $2$  K a saturation of the magnetization is observed for  $H \geq 0.5$  T and a coercive field about  $3$  mT is observed in the hysteresis loop (inset down in Fig. 2). The saturated magnetic moment extracted from the magnetization measurements at  $1.8$  K is about  $M_S = 1.1 \mu_B/\text{Ce}$ , a value which is clearly smaller than that expected for the free  $\text{Ce}^{3+}$  ion ( $g_J J = 2.14 \mu_B$ ). The Kondo effect reduces both the magnetic moment and the magnetic order [6]. Note that there is no saturation for  $T > 2$  K. For  $T$  between  $T_C$  and  $T_N$  ( $T = 3$  and  $4$  K), the magnetic isotherms are linear with  $H$  up to  $0.04$  and  $0.1$  T, respectively, but a positive curvature increases progressively with increasing field (Fig. 2). This behaviour evidences the existence of a ferromagnetic state below  $T_C \approx 2$  K and an AF state for  $T > 2$  K. These results are in agreement with of neutron diffraction Laffargue et al. [4] who have observed on  $\text{Ce}_2\text{Pd}_{2.06}\text{Sn}_{0.96}$  a change from a ferromagnetic at  $3$  K to an incommensurate AF state at  $4.8$  K, but in contrast with those reported by Gordon et al. [2] who interpreted the  $4.2$  K anomaly as a ferromagnetic state order.

#### 4. Specific heat measurements

The magnetic  $4f$ -derived contribution  $C_{\text{mag}}(T)$  to the total specific heat of  $\text{Ce}_2\text{Pd}_2\text{Sn}$ , obtained by subtracting the phonon contribution ( $\text{La}_2\text{Pd}_2\text{Sn}$ ), is shown in Fig. 3. The thermal variation is characterized by a large jump at  $4.8$  K, followed by a tail at higher temperature. In the ordered phase a small peak at  $2.1$  K, with signs of a first-order characteristic transition, marks the stabilization of a ferromagnetic phase. Below that temperature, there is

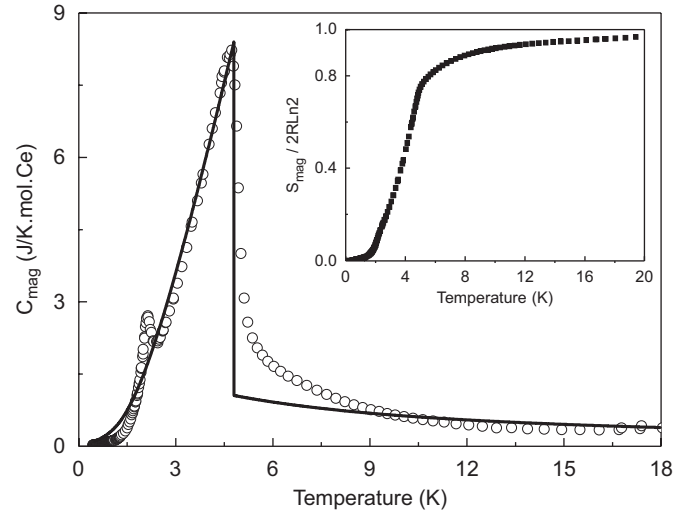


Fig. 3. Specific heat as a function of temperature for  $\text{Ce}_2\text{Pd}_2\text{Sn}$ . Solid line: calculated curve. Inset: associated magnetic entropy gain.

a significant decrease of  $C_{\text{mag}}(T)$  which extrapolates to a quite small value of the electronic  $\gamma_e$  term of about  $5 \text{ mJ/mol K}^2$ .

It is well known that most of Ce-based compounds which adopt magnetic ground states are governed by a competition between Kondo and RKKY magnetic interactions. Since the Kondo effect is basically due to the screening of local moments by conduction-electron spins through a coupling of AF nature, the ordered states driven by these interactions are also expected to be AF [7]. This is observed in most of Ce magnetic compounds, and the few exceptional ferromagnetic-Ce state cases are due to a well-localized  $4f^1$  state with negligible hybridization.

#### 5. Evaluation of Kondo temperature

The low temperature specific heat in the magnetic Kondo compounds, with a doublet crystal-field ground state, are well described within an approach based on molecular field calculations for  $S = 1/2$  resonant level model [8,9]. We have shown [9] that within this framework, a magnetic state is possible only if  $|J_m|/T_K > \pi/2$  ( $J_m$  being the molecular field parameter), with reduced magnetic ground state moments (spontaneous magnetization in the case of a ferromagnetic order or staggered magnetization for a simple antiferromagnet). This model also provides a good description of the thermal variation of the specific heat: it accounts, e.g., for both the shape and the amplitude of the excess specific heat.

Fig. 3 illustrates the experimental zero-field  $C_{\text{mag}}(T)$  variation for  $\text{Ce}_2\text{Pd}_2\text{Sn}$  ( $T_N = 4.8$  K) compared to the calculated curve ( $T_K = 3$  K, solid line;  $T_K/T_N = 0.625$ ). We can also evaluate  $T_K$  from the thermal variation of the entropy  $S_{\text{mag}}(T)$ :  $T_K$  is the temperature where the entropy reaches the  $0.45R \ln 2$  value [10]. This gives  $T_K$  around  $2.9$  K, in very good agreement with the evaluated value

from the calculated curve ( $T_K = 3$  K). The zero-field specific heat jump  $\delta C_{\text{mag}}$  at the magnetic transition  $T_N$  is in very good agreement with the calculated curve. Note that the magnetic contribution  $C_{\text{mag}}$  peaks is 8.23 instead of 12.48 J/K mol Ce, expected for an  $S = 1/2$  two-level system. In this model, the exchange energy  $J_m$  is about twice the magnetic-ordering temperature  $T_N$ , when  $T_K/T_N$  goes to zero:

$$\left(\frac{T_N}{J_m}\right) \rightarrow \frac{1}{2} - \frac{7\zeta(3)}{\pi^3} \left(\frac{T_K}{T_N}\right),$$

where  $\zeta(z)$  is the Riemann zeta function, which would lead to magnetic ordering around  $T_N^* = 6.5$  K, if the Kondo effect is absent. Indeed the characteristic parameters of the magnetic state of Ce are reduced by the Kondo effect.

Using Eqs. (12), (13) and (15) of Ref. [7], we have calculated explicitly the electronic specific heat coefficient value [9]:

$$\gamma_e = \frac{\pi k_B N_A}{3T_K} \frac{1}{1 + ((J_m M(0)/M_0)/T_K)^2} = 209 \text{ mJ/K}^2 \text{ mol},$$

where  $k_B$  and  $N_A$  are the Boltzmann and the Avogadro constants, respectively, and  $M(0)/M_0$  is the spontaneous magnetization,  $T_K$  and  $T_N$  are the fitting parameters.

A comparison with  $T_K$  contrast the widespread claim that  $T_K \sim 1/\gamma_e$ . Rather, the  $\gamma_e$  term depends not only on the  $T_K$  value, but is closely connected to  $T_{\text{RKKY}}$ , at least as long as  $T_K/T_{\text{RKKY}}$  remains in a magnetic solution. Note that in the absence of magnetic order, the Kondo temperature should be

$$T_K^* = \frac{2J_m}{\pi} = 8.3 \text{ K}.$$

Furthermore, an estimation of the electronic specific-heat coefficient from the experimental points data gives  $\gamma_e$  around 100 mJ/K<sup>2</sup> mol, in a qualitative agreement with the calculated value. Estimates of the electronic coefficient of  $\gamma_e$  depend strongly on assumptions made about the importance of crystalline electric-field effects, and about the contribution of the related Schottky anomaly [11]. This  $\gamma_e$  value derived is characteristic for many magnetically ordered Kondo systems, such as the archetype CeAl<sub>2</sub> ( $\gamma = 135$  mJ/K<sup>2</sup> mol) [8].

The numerically calculated values of the specific heat jump  $\delta C_{\text{mag}}$  at  $T = T_N$  in zero external magnetic field are presented in Fig. 4 (solid line). This jump is given as follows [12]:

$$\delta C_{\text{mag}} = \frac{6k_B}{\psi'''(1/2 + \zeta)} \left[ \psi' \left( \frac{1}{2} + \zeta \right) + \zeta \psi'' \left( \frac{1}{2} + \zeta \right) \right]^2,$$

where  $\zeta = (T_K/T_N)/2\pi$  and  $\psi'$ ,  $\psi''$  and  $\psi'''$  are the first, second and third derivatives of the digamma function.

$\delta C_{\text{mag}}$  decreases continuously with increasing  $T_K/T_N$  from the value  $3/2k_B N_A \approx 12.48$  J/K mol for a non-hybridized 4f magnetic system ( $T_K = 0$ ). The characteristic

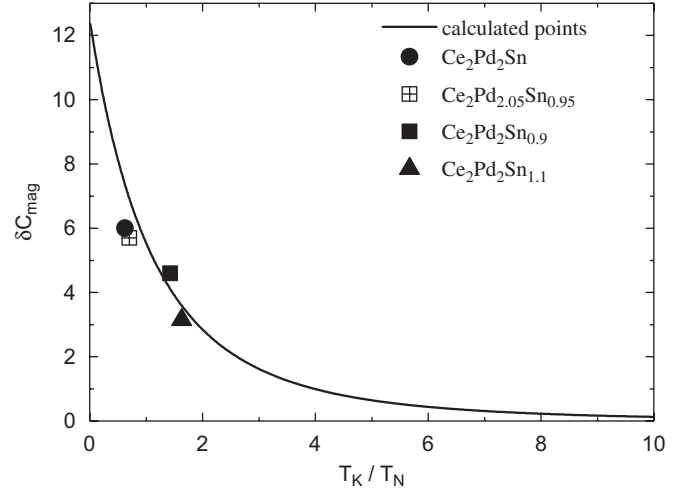


Fig. 4.  $\delta C_{\text{mag}}$  variation of the specific heat jump at the magnetic transition temperature  $T_N$  as a function of the ratio of the two characteristic temperatures  $T_K$  and  $T_N$ .

values obtained in this series match very well with this crude model.

## 6. Conclusions

We have reported that the Ce<sub>2</sub>Pd<sub>2</sub>Sn compound exhibits two magnetic transitions, the upper-ordering temperature,  $T_N = 4.8$  K, shows characteristic features of an antiferromagnetic transition but preceded at higher temperature by magnetic correlations. The lower transition,  $T_C = 2.2$  K, indicates a change in magnetic ground state toward a ferromagnetic type arrangement of the moments.

The  $S = 1/2$  resonant level model leads to trace the temperature-dependent specific heat with only two adjustable parameters:  $T_K$  and  $T_N$ . The fitting curve shown, in Fig. 3, is in very good agreement with the experimental points. Finally, a close relationship between the specific heat jump at the magnetic transition and the  $T_K/T_N$  ratio is demonstrated Fig. 4.

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